DIRECT CALCIUM AND MAGNESIUM ANALYSIS BY A
MODIFIED ATOMIC ABSORPTION SPECTROPHOTOMETRY
ASPIRATION SYSTEM

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INTRODUCTION

The increasing demand for rapid analysis of calcium and magnesium in the study of natural water systems has led to the development of a modified aspiration system for atomic absorption.

In the acetylene-air flame, calcium and magnesium absorbances are lowered due to interferences such as phosphorus (4). The addition of lanthanum or strontium to samples and standards corrects for the chemical interference. Usually a 0.1% to 1.0% solution of lanthanum or strontium is added, volumetrically, to samples. This is time consuming and is a source of error. However, the high levels of calcium and magnesium found in some natural waters require some ratio of dilution to bring them within the linear working range of atomic absorption

The system involved in this study provides one means for the pretreatment and dilution of each natural water sample as it is aspirated directly into the nebulizer. Ward and Biechler (6) have presented a study of interferences using a similar system, but in the nitrous-oxide and acetylene flame.

MATERIALS AND METHODS

The system described here has been termed the Dual Aspiration System (D.A.S.).

The D.A.S. consists of a "T" fitting connected to the nebulizer and is fitted with two polyethylene tubes. Singhal, Sinha and Banerjee (2) and

Singhal and Banerjee (1) have described a method whereby a reagent solution is aspirated through one arm of the "T" while standards or samples are aspirated through the other.

The "T" is available through Elkay Products (No. PT-2). The bottom of the "T" is fitted to the adjustable nebulizer by a short 0.015 inch I.D. polyethylene tube. The two arms of the "T" are then fitted with nine inch lengths of the same tubing. The tubing used is available from Technicon Instruments Corporation and is called "standard pump tubing". The tubing finally selected was the 0.015 inch I.D. size.

An air-acetylene flame was used and the reagent solution consisted of 0.5% La_2O_3 w/v and 2.5% HCl v/v. Standards were prepared from 1000 ppm stock solutions.

INSTRUMENTAL CONDITIONS

All data was obtained using a Perkin-Elmer ATomic Absorption Spectrophotometer Model 306 equipped with a Model 056 Multirange Recorder, and Intensitron[R] Calcium and Magnesium hollow cathode lamps.

The primary wavelengths for calcium (422.7 nm) and magnesium (285.2 nm) were used.

Slit settings were: calcium, 0.7 nm and magnesium, 1.4 nm.

The high concentrations of calcium and magnesium in the samples analyzed in this study required that the burner be rotated approximately 90° to reduce the cell path length.

The flame conditions used were reducing for calcium and oxidizing for magnesium.

The adjustable nebulizer was set at an uptake rate of approximately 2.8 ml/min. for both tubes of the "T" while aspirating deionized water.

INTERFERENCES

Chemical repression of calcium and magnesium in the air-acetylene flame was achieved using the lanthanum solution described above. Samples and standards were treated as described using the D.A.S. The stated per cent solution used for treatment was found to be high enough to arrest the chemical interference, yet not clog the burner slit.

RESULTS AND DISCUSSION

The major concern involving the D.A.S. was reliability. The first investigation involved aspiration rates of various tubing sizes.

A noticeable drop in aspiration rate using the D.A.S. was observed with the 0.015 in. I.D. Technicon$^{(R)}$ tubing. Aspirating with both tubes from a 10 ml graduated cylinder produced an uptake rate of 2.8 ml/min. A rate of 2.8 ml/min. was also observed for a 0.5% La_2O_3/2.5% HCl solution. Attempting to increase the amount of sample introduced to the flame, larger tubing was experimented with. Although the aspiration rate increased, new problems occurred.

A tubing size of 0.030 in. I.D. was found to cause an apparent increase in concentration reading if the sample level was held constant and diluent level was allowed to drop approximately 4.5 inches. A decrease in concentration reading was observed if the diluent side was held constant and the sample level dropped approximately 4.5 inches. Similar results were obtained using a 0.023 in. I.D. tubing. The Technicon $^{(R)}$ 0.015 in. I.D. tubing was found to produce no significant variations (Table I). Throughout this phase of the study an 80 mg/l calcium standard was used. The 80 mg/l calcium standard was again used to obtain four readings over a typical routine analysis. The standard level was held constant and the diluent level varied from full to three-fourths, to one-half, and finally one-fourth. A standard deviation of

1.79, a mean of 83.0 mg/l, and a coefficient of variation of 2.15% was calculated. The diluent was then held constant and the 80 mg/l standard level changed. Three readings (full, half, and three-fourths) gave a standard deviation of 0.83, a mean of 80.6 mg/l, and a coefficient of variation of 1.02%.

Water samples selected at random were analyzed by the conventional single tube aspiration method (4) and the D.A.S. method. Results are given in Table IIa. Percent difference was calculated by assuming that the single aspiration system was the standard value. No significant difference was found. The percent difference range was -5.1 to 4.9 for a calcium concentration range of 7.8 mg/l to 162.0 mg/l. Magnesium percent difference range was -4.0 to 1.0 for a concentration range of 5.0 mg/l to 20 mg/l.

Environmental Protection Agency (E.P.A.) standard reference samples were analyzed as accuracy checks (Table IIb). The E.P.A. values were assumed to be the standard value for percent difference calculations. The D.A.S. appeared to produce better accuracy overall than the single aspiration system. The E.P.A. calcium levels studied were 9.0 mg/l and 36.0 mg/l. The percent difference of the D.A.S. compared with that of the single aspiration system was -6.7 and 6.7 respectively at the 9.0 mg/l level. However, at the 36.0 mg/l level the D.A.S. provided a -5.3 percent difference compared to a 7.2 percent difference of the single aspiration system. Magnesium values at the 2.1 mg/l level were: D.A.S., 4.8% and single aspiration, 4.8%. At the 8.2 mg/l level, the magnesium values were: D.A.S., 0.0% and single aspiration, 4.9%.

Standard deviation, mean, and percent coefficient of variation data were compiled by replicate analyses of a sample periodically run throughout a routine analysis (Table III).

The percent recovery data in Table II was calculated from the formula:

$$\frac{S_a - \frac{1}{2}U_e}{\frac{1}{2}S_k} \quad X \quad 100 = \% \text{ recovery}$$

Where:

S_a is the standard addition experimental value.

U_e is the unknown experimental value

S_k is the known standard value

The formula assumes a 1:1 dilution of an unknown with an appropriate standard.

The working ranges obtained for calcium and magnesium using the D.A.S. were 2.5 mg/l to 160.0 mg/l and 1.0 mg/l to 40.0 mg/l respectively.

It is not known whether the D.A.S. produces an exact 1:1 dilution. However, the dilution ratio is constant and, therefore, normal calibration is not affected.[5]

Leiritie and Mattsson (3) have discussed a modified sample addition method for the analysis of various elements using a similar aspiration system.

CONCLUSION

The D.A.S. as a peripheral tool to atomic absorption spectrophotometry appears to have added a useful dimension to an already powerful analytical technique and is adaptable to the analysis of natural waters.

The tubing size is a major factor in the performance of the system as was shown. Using the correct tubing size satisfactorily eliminates head pressure effects found with larger tubing.

The D.A.S. method of direct analysis for Ca and Mg provides for the simultaneous chemical treatment thus avoiding any pretreatment with its associated errors.

The overall performance of the D.A.S. for high concentrations of calcium

and magnesium has been shown to be as reliable as the single aspiration system (Table II). The D.A.S. method of analysis is being used routinely in this laboratory with great success. Quality control measures (i.e. standard additions and independent standard reference samples) have shown the system to be reliable.

Two other parameters which are found in high concentrations in some natural waters are sodium and potassium. This laboratory is analyzing these parameters routinely using the D.A.S. The D.A.S. is being used in this instance as a dilution device to accommodate the high concentrations of sodium and potassium found in the samples studied.

REFERENCES

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TABLE I

COMPARISON OF PERCENT CHANGE IN SAMPLE CONCENTRATION WITH RESPECT TO TUBING INSIDE DIAMETER

Tubing Size	% Apparent Increase in Concentration (Sample Level Held Constant)	% Apparent Decrease in Concentration (Diluent Level Held Constant)
Technicon[R] 0.015 in. I.D.	0.56	2.47
Intramedic[R] 0.023 in. I.D.	12.46	13.26
Technicon[R] 0.030 in. I.D.	14.06	13.70

TABLE II

CALCIUM-MAGNESIUM DATA COMPARISON IN NATURAL WATERS (mg/1)

A.

Element: Calcium

Sample No.	Dual Aspiration Value	Single Aspiration Value	% Difference
H120	46.0	47.2	2.5
H122	81.1	81.2	0.1
R166	53.2	54.8	2.9
I502	8.9	8.6	-3.5
F1104	23.2	24.4	4.9
F1108	8.2	7.8	-5.1
F1112	66.4	64.8	-2.5
F1114	63.9	64.2	0.5
E041	39.6	38.8	-2.1
A224	160.3	162.0	1.0

Element: Magnesium

Sample No.	Dual Aspiration Value	Single Aspiration Value	% Difference
YB694	15.4	14.9	-3.4
YB698	6.3	6.3	0.0
YB702	19.8	20.0	1.0
B498	15.7	15.1	-4.0
B510	5.2	5.0	-4.0
YC719	14.7	14.2	-3.5
YC739	15.0	14.6	-2.7

B.

Element	EPA Value	Dual Aspiration Value	% Difference	Single Aspiration Value	% Difference
Calcium	9.0	9.6	-6.7	8.4	6.7
	36.0	37.9	-5.3	33.4	7.2
Magnesium	2.1	2.0	4.8	2.0	4.8
	8.2	8.2	0.0	7.8	4.9

TABLE III

STATISTICAL DATA COMPUTED ON RANDOMLY CHOSEN
NATURAL WATER SAMPLES, ANALYZED BY THE D.A.S.

Element: Calcium

Sample No.	n	$\overline{X}$	% C.V.	Ue	Sk	Sa	% Recovery
YB694	3	48.3	0.8	48.8	100.0	79.6	110.4
YA703	8	44.7	2.7	43.5	50.0	47.8	104.2

Element: Magnesium

Sample No.	n	$\overline{X}$	% C.V.	Ue	Sk	Sa	% Recovery
YB694	3	15.4	0.8	15.4	30.0	22.5	98.7
YA703	4	15.1	0.5	15.1	20.0	17.5	99.5

n   =   number of sample repeats

$\overline{X}$ =   sample average

% C.V.=   coefficient of variation

Ue, Sk, Sa, % recovery = all defined within text

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